

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

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PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing
(day/month/year)

12.11.2004

Applicant's or agent's file reference
SMC 60539/WO

IMPORTANT NOTIFICATION

International application No.
PCT/GB 03/03345

International filing date (day/month/year)
30.07.2003

Priority date (day/month/year)
28.08.2002

Applicant
AVECIA LIMITED et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

Name and mailing address of the international
preliminary examining authority:



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PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT (PCT Article 36 and Rule 70)

Applicant's or agent's file reference SMC 60539/WO	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416)	
International application No. PCT/GB 03/03345	International filing date (<i>day/month/year</i>) 30.07.2003	Priority date (<i>day/month/year</i>) 28.08.2002
International Patent Classification (IPC) or both national classification and IPC C09B47/04		
Applicant AVECIA LIMITED et al.		
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of 5 sheets.</p>		
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> I <input checked="" type="checkbox"/> Basis of the opinion II <input type="checkbox"/> Priority III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input checked="" type="checkbox"/> Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input type="checkbox"/> Certain documents cited VII <input type="checkbox"/> Certain defects in the international application VIII <input type="checkbox"/> Certain observations on the international application 		
Date of submission of the demand 22.01.2004	Date of completion of this report 12.11.2004	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Fritz, M Telephone No. +49 89 2399-2792	



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB 03/03345

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

1-38 as originally filed

Claims, Numbers

1-26 received on 05.08.2004 with letter of 05.08.2004

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

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**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes: Claims	1-26
	No: Claims	
Inventive step (IS)	Yes: Claims	1-26
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-26
	No: Claims	

2. Citations and explanations

see separate sheet

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

D3: GB-A-2 237 284 (MINNESOTA MINING & MFG) 1 May 1991 (1991-05-01) cited in the application

The present application describes phthalocyanine compounds of the general formula I (claims 1-13), methods involving the compounds I (claims 14-19,21,26), an article comprising a compound I (claim 20), an ink comprising a compound I (claims 22-24) as well as the use of a compound I as a security marker (claim 25).

The title compound according to ex. 9 of D3 is a representative of the compounds I according to the present case, however excluded by the subject-matter of the claims by a proviso.

The novelty of claims 1-26 is therefore acknowledged (Art. 33(2) PCT).

Closest prior art is D3.

The problem of the present application was to provide further metaloxypthalocyanine compounds absorbing in the near infrared region of the electromagnetic spectrum.

It is evident from the description that this problem is solved.

Example 9 of D3 refers to a compound which is a representative of the compounds I according to the present case, however D3 (cf. claim 1) teaches that "one and only one of Y and Z on each ring unit must be other than H" so that example 9 of D3 discloses a compound which is not within the subject-matter of the claims of this document.

In contrast thereto the compounds I of the present case are defined as having 8 identical non-hydrogen substituents corresponding to the groups Y and Z in the compounds (I) of D3.

Because of the teaching apparent in the claims of D3, the skilled man being aware of this document would not have considered to generalize example 9 (which would have been necessary to arrive at the compounds I of the present case).

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB 03/03345

The compounds I according to the present case are - by consequence - not obvious for the skilled man, and an inventive step in the sense of Art. 33(3) PCT is acknowledged for the subject-matter of claims 1-26.

Further objections:

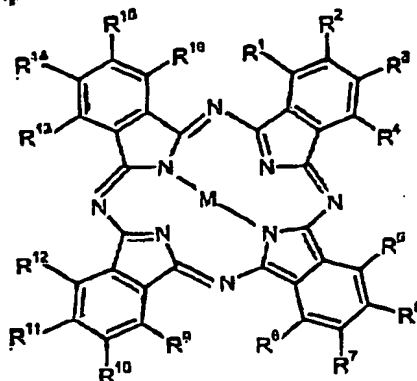
The description was not adapted to the amended claims as requested by Article 6 PCT. This could be done in an eventual National / European Phase of examination.

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DT12 Rec'd PCT/PTO 25 FEB 2005

CLAIMS - AMENDED

1. A phthalocyanine compound of Formula I



wherein at least the eight groups represented by R^1 , R^4 , R^5 , R^8 , R^9 , R^{12} , R^{13} & R^{16} which groups are identical are $-X-J$ wherein

J is selected from C_{1-8} -alkyl; C_{2-8} -alkenyl; C_{4-8} -cycloalkyl (each being optionally substituted by a group selected from C_{1-4} -alkoxy, C_{1-4} -alkylthio, C_{8-12} -aryl, C_{8-12} -arylthio, C_{1-4} -alkylsulphonyl, C_{1-4} -alkylsulphonylamino, C_{1-4} -alkylsulphoxide, amino, mono- and di- C_{1-4} -alkylamino, halogen, nitro, cyano and hydroxycarbonyl ($-COOH$), hydroxysulphonyl ($-SO_3H$) or dihydroxyphosphonyl ($-PO_3H_2$) or C_{1-4} -alkyl esters thereof) and from C_{8-12} -aryl (optionally substituted by a group selected from C_{1-3} -alkyl, C_{1-3} -alkoxy, C_{1-3} -alkylthio, C_{1-3} -alkylsulphonyl, C_{1-3} -alkylsulphonylamino, C_{1-4} -alkylsulphoxide, amino, mono- and di- C_{1-3} -alkylamino, halogen, nitro, cyano and hydroxycarbonyl, hydroxysulphonyl or dihydroxyphosphonyl, hydroxycarbonyl- C_{1-3} -alkyl, hydroxysulphonyl- C_{1-3} -alkyl, dihydroxyphosphonyl- C_{1-3} -alkyl or C_{1-3} -alkyl esters thereof);

M is an oxymetal group selected from VO, TiO and MoO;

X is S, Se, Te or NT;

T is H, alkyl or phenyl, or T & J, together with the N atom to which they are attached, form an aliphatic or aromatic ring provided this N atom is not positively charged; provided where J is aryl, T is not aryl;

and the remaining groups from R^1 to R^{16} are independently selected from H, halogen, $-OJ$, hydroxycarbonyl, hydroxysulphonyl, dihydroxyphosphonyl, hydroxycarbonyl- C_{1-3} -alkyl, hydroxysulphonyl- C_{1-3} -alkyl and dihydroxyphosphonyl- C_{1-3} -alkyl, provided that at least one of R^2 and R^3 , at least one of R^8 and R^7 , at least one of R^{10} and R^{11} and at least one of R^{14} and R^{15} is hydrogen, with the proviso that the compound is not octa-3,6-(phenylthio)VOPc, octa-3,6-(methylthio)TiOPc or octa-3,6-(ethylthio)VOPc.

2. A phthalocyanine compound according to Claim 1 wherein each of R^2 , R^3 , R^8 , R^7 , R^{10} , R^{11} , R^{14} & R^{15} is H.

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AMENDED SHEET

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3. A phthalocyanine compound according to any one preceding Claim wherein the compound has an electronic absorption peak from 750 to 1100 nm, more preferably from 800 to 1000 nm.
- 5 4. A phthalocyanine compound according to Claim 3 wherein the compound has at least 90%, preferably at least 95%, of its absorption strength in the region above 400nm at or above 750 nm.
- 10 5. A phthalocyanine compound according to Claim 3 or 4 wherein the electronic absorption peak has a band width at half peak height in solution of less than 60 nm.
- 15 6. A phthalocyanine compound according to any one preceding Claim wherein J is selected from C₃₋₆-alkyl, which may be straight or branched chain; C₂₋₄-alkenyl; cyclohexyl; phenyl; naphtha-1-yl or naphtha-2-yl, each of which is optionally substituted as defined in claim 1.
- 20 7. A phthalocyanine compound according to Claim 6 wherein J is phenyl, optionally substituted as defined in claim 1.
- 25 8. A phthalocyanine compound according to Claim 6 or 7 wherein the substituent(s) for the phenyl; naphtha-1-yl or naphtha-2-yl groups represented by J is(are) independently selected from C₁₋₂-alkyl; C₁₋₂-alkoxy; C₁₋₂-alkylthio; C₁₋₂-alkylsulphonyl; C₁₋₂-alkylsulphoxide; amino; mono- and di-C₁₋₂-alkylamino; halogen; nitro; cyano; hydroxycarbonyl, hydroxysulphonyl, dihydroxy-phosphonyl, hydroxycarbonyl-C₁₋₃-alkyl, hydroxysulphonyl-C₁₋₃-alkyl and dihydroxy-phosphonyl-C₁₋₃-alkyl and C₁₋₂-alkyl esters thereof.
- 30 9. A phthalocyanine compound according to any one of claims 6 to 8 wherein the optionally substituted phenyl; naphtha-1-yl or naphtha-2-yl groups represented by J are selected from phenyl, 4-methylphenyl, 2-methylphenyl, 4-1-propylphenyl, 2,4-dimethylphenyl, 2,5-dimethylphenyl, 3,5-dimethylphenyl, 4-methoxyphenyl, 4-methylthiophenyl, 3-(2-[methoxycarbonyl]ethyl)phenyl, 3-(hydroxycarbonyl)phenyl, 4-(hydroxysulphonyl)-phenyl, 2-chlorophenyl, 4-bromophenyl, 3,5-dichlorophenyl, naphtha-1-yl and naphtha-2-yl.
- 35 10. A phthalocyanine compound according to any one of the preceding claims wherein the compound has a formula:
- octa-3,6-(RX)-Pc-M Formula III
- wherein
- 40 M is an oxymetal group selected from VO, TiO and MoO;

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Pc is the phthalocyanine nucleus;

X is S, Se, Te or NT wherein T is H, C₁₋₄-alkyl or phenyl; and

R is phenyl or naphthyl each of which is optionally substituted by up to 5 groups selected from C₁₋₃-alkyl, C₁₋₃-alkoxy, C₁₋₃-alkylthio, C₁₋₃-alkylsulphonyl, C₁₋₃-alkylsulphonyl-amino, C₁₋₃-alkylsulphoxide, amino, mono- and di-C₁₋₃-alkylamino, halogen, nitro, cyano and hydroxycarbonyl, hydroxy-sulphonyl, dihydroxyphosphonyl, hydroxycarbonyl-C₁₋₃-alkyl, hydroxysulphonyl-C₁₋₃-alkyl or hydroxyphosphonyl-C₁₋₃-alkyl or C₁₋₃-alkyl esters thereof, or

R & T together form a piperidiny, piperaziny, morpholiny or pyrroliny ring.

11. A phthalocyanine compound according to any one of the preceding claims wherein X is sulphur.

12. A phthalocyanine compound according to any one preceding Claim wherein each of R¹, R⁴, R⁵, R⁸, R⁹, R¹², R¹³ & R¹⁸ is 4-methylphenylthio and each of R², R³, R⁶, R⁷, R¹⁰, R¹¹, R¹⁴ & R¹⁵ is H.

13. A phthalocyanine compound according to any one preceding Claim wherein M is VO.

14. A method for the production of a lithographic printing plate containing a photosensitive layer comprising irradiating the photosensitive layer with an infra-red laser in accordance with pattern information wherein the photosensitive layer comprises a compound of formula I in claim 1 without the proviso that the compound is not octa-3,6-(phenylthio)VOPc, octa-3,6-(methylthio)TiOPc or octa-3,6-(ethylthio)VOPc.

15. A method of polymer welding in which a polymer material is irradiated with infra-red laser in a region where it is desired to form a weld wherein the polymer material comprises a compound of formula I in claim 1 without the proviso that the compound is not, octa-3,6-(phenylthio)VOPc, octa-3,6-(methylthio)TiOPc or octa-3,6-(ethylthio)VOPc, or wherein the polymer material is coated or printed with the compound where it is desired to form a weld, or wherein the compound is provided in a layer or film which is located adjacent the polymer material where it is desired to form a weld.

16. A method for the protection of an interior of a glazed structure against the heating effect of incident IR radiation by incorporating into the glazing or a layer forming part of the glazing a compound of formula I in claim 1 without the proviso that the compound is not octa-3,6-(phenylthio)VOPc, octa-3,6-(methylthio)TiOPc or octa-3,6-(ethylthio)VOPc.

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17. A method for the attenuation of IR irradiation passing through a protective film by incorporating into the protective film or a layer forming part of the protective film an compound of formula I in claim 1 without the proviso that the compound is not octa-3,6-(phenylthio)VOPc, octa-3,6-(methylthio)TiOPc or octa-3,6-(ethylthio)VOPc.

18. A method for detecting an article carrying a superficial image by scanning with an infra-red detector wherein the image comprises a compound of formula I in claim 1 without the proviso that the compound is not octa-3,6-(phenylthio)VOPc, octa-3,6-(methylthio)TiOPc or octa-3,6-(ethylthio)VOPc.

19. A method for the formation of a permanent toner image on a substrate using an electrophotographic device incorporating an IR source to fix the temporary toner image on the substrate and/or provide an IR-readable permanent toner image wherein the toner comprises a compound of formula I in claim 1 without the proviso that the compound is not octa-3,6-(phenylthio)VOPc, octa-3,6-(methylthio)TiOPc or octa-3,6-(ethylthio)VOPc.

20. An article carrying an image adapted for machine reading in response to a reflective signal generated by scanning the image with infra-red radiation wherein the image comprises a compound of formula I in claim 1 without the proviso that the compound is not octa-3,6-(phenylthio)VOPc, octa-3,6-(methylthio)TiOPc or octa-3,6-(ethylthio)VOPc.

21. A method for the enhancement of a thermal signal comprising incorporating into or onto the article from which the thermal signal is derived a compound of formula I in claim 1 without the proviso that the compound is not octa-3,6-(phenylthio)VOPc, octa-3,6-(methylthio)TiOPc or octa-3,6-(ethylthio)VOPc.

22. An ink comprising a compound of formula I in claim 1 without the proviso that the compound is not octa-3,6-(phenylthio)VOPc, octa-3,6-(methylthio)TiOPc or octa-3,6-(ethylthio)VOPc.

23. An ink according to Claim 22 also comprising a colorant.

24. An ink according to Claim 22 or Claim 23 also comprising an alkoxylated or polyalkoxylated acrylate monomer and a photoinitiator.

25. Use of compounds of formula I in claim 1 but without the proviso that the compound is not octa-3,6-(phenylthio)VOPc, octa-3,6-(methylthio)TiOPc or octa-3,6-(ethylthio)VOPc as a security marker.

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26. A method of establishing the authenticity of an article or substrate comprising marking the article or substrate with a mark including a compound according to formula I in claim 1 without the proviso that the compound is not octa-3,6-(phenylthio)VOPc, octa-3,6-(methylthio)TiOPc or octa-3,6-(ethylthio)VOPc and detecting and/or measuring a
5 characteristic absorption of infrared radiation by the mark.

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